Design and Evaluation of a Crystalline Hybrid of Molecular Conductors and Molecular Rotors

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Résumé en anglais	Combining recent concepts from the fields of molecular conductivity and molecular machinery we set out to design a crystalline molecular conductor that also possesses a molecular rotor. We report on the structures, electronic and physical properties, and dynamics of two solids with a common 1,4-bis(carboxyethynyl)bicyclo[2.2.2]octane (BABCO) functional rotor. One, [nBu(4)N(+)](2)[BABCO][BABCO(-)](2), is a colorless insulator where the dicarboxylic acid cocrystallizes with two of its monoanionic conjugated bases. The other is self-assembled by electrocrystallization in the form of black, shiny needles, with highly conducting molecular slabs of (EDT-TTF-CONH2)(2+) (EDT-TTF = ethylenedithiotetrathiafulvalene) and anionic [BABCO(-)] rotors. Using variable-temperature (5-300 K) proton spin lattice relaxation, H-1 T-1(-1), we were able to assign two types of Brownian rotators in [nBu(4)N(+)](2)[BABCO(-)][BABCO(-)](2). We showed that neutral BABCO groups have a rotational frequency of 120 GHz at 300 K with a rotational barrier of 2.03 kcal mol(-1). Rotors on the BABCO- sites experience stochastic 32 GHz jumps at the same temperature over a rotational barrier of 2.72 kcal mol(-1). In contrast, the BABCO(-) rotors within the highly conducting crystals of (EDT-TTF-CONH2)(2)(+)[BABCO(-)] are essentially braked at room temperature. Notably, these crystals possess a conductivity of 5 S cm(-1) at 1 bar, which increases rapidly with pressure up to SOS cm(-1) at 11.5 kbar. Two regimes with different activation energies Ea for the resistivity (180 K above 50 and 400 K below) are observed at ambient pressure; a metallic state is stabilized at ca. 8 kbar, and an insulating ground state remains below 50 K at all pressures. We discuss two likely channels by which the motion of the rotors might become slowed down in the highly conducting solid. One is defined as a low-velocity viscous regime inherent to a noncovalent, physical coupling induced by the cooperativity between five C-sp3-H center dot center dot center dot O hydrogen bonds engaging any rotor and five BABCO units in its environment. The rotational barrier calculated with the effect of this set of hydrogen bonds amounts to 7.3 kcal mol(-1). Another is quantum dissipation, a phenomenon addressing the difference of dynamics of the rotors in the two solids with different electrical properties, by which the large number of degrees of freedom of the low dimensional electron gas may serve as a bath for the dissipation of the energy of the rotor motion, the two systems being coupled by the Coulomb interaction between the charges of the rotors (local moments and induced dipoles) and the charges of the carriers.
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